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(translated by Jeekai)

Invention Title:

Cement Retarder and Its Manufacture Method

Abstract:

A new, high effective cement retarder having super low viscosity for cementing of oil (gas) well and its manufacture method are provided. Highly degraded, refined cotton cellulose, sodium chloroacetate, caustic soda, methanol etc are used as raw material, then neutralized and washed by methanol solution and added hydrochloric acid to obtain methanol-modified carboxymethyl cellulose salt having super low viscosity, namely, the cement retarder of the present invention. Said cement retarder is added to cement slurry and thus obtain various good characteristics, such as good retarding effect, rapid dissolution, low viscosity, good fluidity, temperature resistance, deformation resistance under pressure etc, which meet safe working requirements of cementing of oil (gas) well, especially deep (hot) well.

Claims:

1 . A cement retarder (referred as retarder hereafter) used for cementing of oil (gas) well, which uses cellulose as basic backbone and is made of cotton cellulose, caustic soda, hydrochloric acid and water etc, characterized in that highly degraded, refined cotton cellulose is used as raw material, sodium chloroacetate as etherifying agent, the resulting carboxymethyl cellulose salt having super low viscosity (initial product of said retarder) should be neutralized and washed by methanol solution along with added hydrochloric acid, and said retarder must contain methanol.

2. The retarder according to claim 1, characterized by following ranges of formulation (based on the refined cotton cellulose):

Refined cotton cellulose	1 part (by weight)
Caustic soda	0.5-0.7 part (by weight)
Sodium chloroacetate	0.87-1.07 parts (by weight)
Water	2.2-3.1 parts (by weight)
Methanol	0.77-1.37 parts (by weight)
Hydrochloric acid	0.4-0.3 part (by weight) .

3. The retarder according to claim 1 or claim 2, characterized in that processing conditions of the method of the present invention are:
(1) Alkalization temperature for spaying alkaline process is 30-35□, time period is 1.5-2 hour, concentration of the caustic soda is 20-22%,
(2) Temperature for etherification of basic cellulose by sodium chloroacetate is 30-40□ during the first 30 minutes, and 40-60□ during last 60 minutes,
(3) Time period for washing initial product by methanol solution and hydrochloric acid is 1-1.5 hours, and concentration of methanol is 70-80%.

4. The retarder according to claim 1 or claim 2, characterized in that said highly degradation is mean that degree of polymerization for refined cotton cellulose is less than 400.

Description:

The present invention relates to a new, high effective cement retarder (referred as retarder hereafter) having super low viscosity for cementing of oil (gas) well, especially deep (hot) well.

The time for solidification of the cement slurry useful for oil wells not only depends on the chemical and physical performance of cement itself, but also is closely related with the environment (temperature and pressure etc.) in which the cement is solidified as well as additives for cement slurry. Among these, a cement retarder as an additive appears to be particularly important for worker in working place to adjust solidification performance of cement slurry.

Well known and commonly used cement retarders used for cementing of oil (gas) well are tannic acid, ferric chromic salt, tartaric acid, sulfonated tannin and hydroxyethyl saponin gum and so on. In the past years, working temperature of cement slurry is increased significantly (often above 100□) with yearly increase in depth of well being drilled and continue elevation in stratum temperature (circulating temperature of slurry). Therefore, the above-described cement retarders can not meet new requirements any more. Among them, for example, tartaric acid has so strong sensitivity that an increase of 0.01% in the added amount will result in dramatic change of time for solidification of cement slurry. And the added amount less than 0.1% even causes accelerating solidification. Meanwhile, the addition of the additive has shortcoming of extracting water largely. And unsuitably-controlled addition of additive is prone to result in failure of working of cementing well. Tannic acid and ferric chromic salt have good retarding effect on cement slurry at 75□. However, both have bad effect at elevated temperature and generally only suitable for the temperature range of less than 80□. Moreover, the much more foam of ferric chromic salt will destroy the quality of well cementing. Hydroxyethyl saponin gum has good temperature resistance and retarding performance, however, high viscosity of its solution (the viscosity for 2% solution is 82.5 centipoises) will affect the fluidity of cement slurry, and often can not be used alone. Ordinary carboxymethyl cellulose can retard the

solidification of cement slurry; however it was only reported in a few documents in China and other countries. It has no practical value and is not suitable to be popularized due to its high viscosity (the viscosity for 2% solution is 100-250 centipoises), which result in significant deterioration in fluidity of cement slurry. (See, <The experimental study report of CD-CMC cement retarder of super low viscidity>, from Eastern Sichuan Petroleum Drilling Company, Sichuan province, China, 1983).

An object of the present invention is to provide a new cement retarder and the method to produce the same. The cement retarder produced by the method can be used as additive for cement slurry to make cement have good fluidity, good retarding property and strong stability to resist temperature, which can meet working requirements of cementing of oil (gas) well, especially deep (hot) well.

The solution of the present invention is that cotton cellulose is used as basic backbone, and a special method is used to make highly degraded methanol-containing carboxymethyl cellulose salt having super low viscosity, namely, the new, high effective cement retarder having super low viscosity according to the present invention. The special preparation procedure is described as follows.

I. Raw material formulations used in the present invention and requirement:

1. Refined cotton cellulose: water content is 6-10%, the degree of polymerization is less than 400, the amount used is 1 part (by weight), and used as basis for calculation;
2. Caustic soda: concentration is 20-22%, the amount used is 0.5-0.7 part (by weight);
3. Sodium chloroacetate: the amount used is 0.87-1.07 part (by weight);
4. Water: the amount used is 2.2-3.1 parts (by weight);
5. Methanol: concentration is less than 75%, the amount used is 0.77-1.37 parts (by weight);
6. Hydrochloric acid: concentration is 31-36%, the amount used is 0.4-0.8 part (by weight).

II. The preparation procedure of the present invention:

1. Refined cotton cellulose is alkalized by spaying alkaline process with caustic soda, to produce alkaline cellulose, with alkalization temperature being 30-35□, time period 1.5-2 hours.
2. The alkaline cellulose is etherified by sodium chloroacetate to produce carboxymethyl cellulose salt having super low viscosity, that is, initial product of the retarder of the present invention. Etherification time is 1.5-2 hours, and temperature is 30-40□ during the first 30 minutes, and 40-60□ during last 60 minutes.
3. The initial product is neutralized and washed by methanol solution and added hydrochloric acid. Time for washing is 1-1.5 hours, and temperature for washing is room temperature.
4. The washed product is centrifuged, dried, crushed to obtain eligible product, that is, cement retarder having super low viscosity of the present invention.

The carboxymethyl cellulose salt having super low viscosity (containing methanol) produced in the present invention has solubility of less than 6 minutes, viscidity of less than 5 centipoises, and pH of 6-7. Its initial solidification time can be more than 6 hours under various temperature and pressure. The reasons for above properties is that highly degraded cellulose has significantly reduced molecular weight, which make molecular colloid adhere to surface of cement particle to form stronger hydration (protective colloid effect), retarding significantly the time for solidification of cement slurry. The shortcomings that moderately viscous retardant building slurry has big glutinousness and bad fluidity etc are overcome due to low viscidity of carboxymethyl cellulose salt produced in the present invention. Many tests and uses have demonstrated that the retarding performance of the retarder of the present invention is good with the change of the added amount. The resisted temperature may be more than 130□, and the pressure may be up to 4.5 atmospheric pressures. Its use in shallow, moderately deep or deep (hot) well can provide reliable assurance to safe working. Further, the method, raw materials and equipments used in the present invention are all those used in common production in chemical industry. Compared with well-known

retarders described above, the retarder according to the present invention has some advantages such as low cost, less amount used, thereby significantly reducing drilling cost.

Example of the present invention:

100g refined cotton cellulose having 6-10% water content and degree of polymerization less than 400, is alkalized by spaying alkaline process with 270g caustic soda having concentration of 22% at alkalization temperature of 30□ for 2 hours. Resulting alkaline cellulose is etherified by 105g sodium chloroacetate to produce carboxymethyl cellulose salt having super low viscosity, that is, initial product of the retarder. The initial product is then neutralized and washed by methanol solution with concentration of 75% and an amount five times initial product by weight, and added hydrochloric acid, to contain methanol. At last, the washed product is centrifuged, dried, and crushed to obtain purely white flocculent cellulose substance, that is, the cement retarder having super low viscosity of the present invention. The resulting cement retarder is used in cement slurry of oil-producing well in Leshan, Sichuan province, China. When the ratio of water to ash is 50%, and the retarder is added in an amount of 0.1%, 0.2% and 0.3% in water, test temperature is 120□, the initial solidification time is 5 hours and 32 minutes, 6 hours and 28 minutes, 7 hours and 18 minutes respectively, and the viscidity is all less than 4 centipoises, pH is 6-7, and fluidity is all 26 cm.